

SEPARATOR FOR NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY, AND  
NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a separator used for a non-aqueous electrolyte secondary battery and a non-aqueous electrolyte secondary battery.

Description of the Related Art

In recent years, portable information instruments, such as a personal computer, a portable telephone and an information terminal, have been widely used. Since these instruments have various multimedia functions, it is therefore desirable that the secondary battery used for such power supply is small and light in weight having a large capacity, namely, a high energy density. At this point, aqueous solution type secondary batteries, such as a conventional lead storage battery and a nickel cadmium storage battery, are not sufficient. Lithium secondary batteries which can realize a higher energy density, especially lithium secondary batteries using as a cathode active material, a composite oxide of lithium, such as lithiated cobalt dioxide, lithiated nickel dioxide, and spinel lithium manganese oxide, and as an anode active material, a carbonaceous material that can be doped/undoped with a lithium ion, have been

developed actively.

Since these lithium secondary batteries have inherently a large energy, improved safety is required against exothermal abnormalities, such as an internal short circuit and an external short circuit. For example, when heat generation occurs in a separator comprising a polyolefin microporous layer, the polyolefin layer is made to have less porous structure at about  $80^{\circ}\text{C}$  -  $180^{\circ}\text{C}$ , and form a structure in which lithium ions are not passed and current of the battery is stopped, thus the safety is improved. (Hereafter, "a microporous layer, such as a polyolefin layer, forms a less porous structure at a time of heat generation and stops current of a battery" may be referred to as "having shut-down function"). However, when a heat generation is still large, there is a problem that the separator itself deformed.

Preparations of a separator have been studied by combining a microporous material mainly comprising polyolefin as a shut-down layer with a heat-resistant porous material. For example, JP-A 11-144697 describes a separator comprising a polyolefin porous film and a polyimide porous film. But there is a problem that the electrochemical oxidation of a heat-resistant porous material occurs during charging/discharging in non-aqueous electrolyte secondary battery.

The object of the present invention is to provide a separator for non-aqueous electrolyte secondary battery containing a heat-resistant microporous layer, which has a shut-down function and excellent electrochemical oxidation resistance, and a non-aqueous electrolyte secondary battery containing the separator.

#### SUMMARY OF THE INVENTION

As a result of extensive studies, the present inventors found out that the above object is attainable by using a separator containing a layer having shut-down function, and a heat-resistant microporous layer, said separator has further a spacer on the surfaces of the heat-resistant microporous layer, and accomplished the present invention.

Namely, the present invention relates to a separator for non-aqueous electrolyte secondary battery, wherein the separator comprises a shut-down layer, a heat-resistant microporous layer, and a spacer on the surface of the heat-resistant microporous layer, and the spacer has a form of particles, fibers, net or porous film. The spacer is disposed on the other surface side of the heat-resistant microporous layer where the shut-down layer is disposed. (Hereinafter, said surface side may be referred to as an external surface.)

Moreover, the present invention relates to a non-aqueous electrolyte secondary battery including the above separator.

#### DETAILED DESCRIPTION OF THE INVENTION

The separator for non-aqueous electrolyte secondary battery of the present invention is characterized by containing a shut-down layer and a heat-resistant porous layer, wherein said separator has a spacer having a form of particles, fibers, net or porous film. In the separator of the present invention, the heat-resistant porous layer suitably consists of a heat-resistant resin, and is suitably adjacent to the shut-down layer.

The shut-down layer of the present invention is not especially limited as long as it has a shut-down function, and it is usually a microporous layer comprising a thermoplastic resin.

As the size of the pore (vacant space) in the shut-down layer, when said pore can be regarded approximately as a spherical form, the diameter of the sphere (hereinafter, it may be referred to as a pore diameter) is suitably  $3\ \mu\text{m}$  or less, and more suitably  $1\ \mu\text{m}$  or less. If the average size or the pore diameter exceeds  $3\ \mu\text{m}$ , a problem of short circuit may easily occur when the carbon powder or the bit which is the main component of a cathode or an anode drops out. As for the size of pores, as long as either one of those of the heat-resistant porous layer or the shut-down layers satisfies the above-mentioned conditions, and the other one may be over  $3\ \mu$

m.

The pore rate (percentage of pore) of the shut-down layer is suitably 30 to 80 volume %, and more suitably 40 to 70 volume %. When the pore rate is less than 30 volume %, the retention amount of an electrolyte may decrease. When the pore rate is more than 80 volume %, the strength of the shut-down layer may become insufficient, and the shut-down function may deteriorate sometimes.

The thickness of the shut-down layer is suitably 3 to 30  $\mu\text{m}$ , and more suitably 5 to 20  $\mu\text{m}$ . When the thickness is less than 3  $\mu\text{m}$ , the shut-down function may be insufficient. When the thickness is more than 30  $\mu\text{m}$ , the thickness including the heat resistant porous layer becomes too thick as a separator for non-aqueous electrolyte secondary battery to obtain a high electric capacity.

It is suitable that the shut-down layer serves as a layer of substantially non-porous at a temperature of 80°C to 180°C. As the thermoplastic resin for the shut-down layer is suitably a thermoplastic resin which softens at 80-180 °C to blockade the pores, and does not dissolve in an electrolyte. Specifically, a polyolefin, a thermoplastic polyurethane, etc. are exemplified. As the polyolefin, more suitable is at least a thermoplastic resin selected from the group consisting of polyethylene, such as low-density polyethylene, high-density

polyethylene, and ultra-high molecular weight polyethylene; polypropylene, and the like.

As the heat-resistant resin which forms a heat-resistant porous layer is suitably at least one heat-resistant resin selected from resins having a temperature of deflection under load according to JIS K 7207 measured at 18.6kg/cm<sup>2</sup> load of 100° C or more. In order to be safer under still severe use at a high temperature, the heat-resistant resin of the present invention, is more suitably at least one heat-resistant resin selected from resins having a temperature of deflection under load of 200° C or more.

Examples of the resins having a temperature of deflection under load of 100° C or more include polyimide, polyamideimide, aramid, polycarbonate, polyacetal, polysulfone, polyphenyl sulfide, polyetherether ketone, aromatic polyester, polyether sulfone, polyether imide, etc. Examples of the resins having a temperature of deflection under load of 200° C or more include polyimide, polyamideimide, aramid, polyethersulfone, polyether imide, etc. Furthermore, as the heat-resistant resin, it is especially preferable to select from the group consisting of polyimide, polyamideimide and aramid.

Moreover, as the heat-resistant resin, it is suitable that a limiting oxygen index is 20 or more. The limiting oxygen index is a minimum oxygen concentration in which a test piece

put into a glass pipe can continue burning. As the heat-resistant porous layer, it is suitably flame retardant in addition to heat resistant in view of oxygen generation from a cathode material at a high temperature. As a concrete example of such a resin, the above-mentioned heat-resistant resins are exemplified.

As the pore size or pore diameter of the above-mentioned heat-resistant porous layer, is suitably 3  $\mu\text{m}$  or less, and more suitably 1  $\mu\text{m}$  or less. If the average pore size or pore diameter exceeds 3  $\mu\text{m}$ , a problem of short circuit may easily occur when the carbon powder or the bit which is the main component of a cathode or an anode drops out.

The pore rate of the heat-resistant porous layer is suitably 30 to 80 volume %, and more suitably 40 to 70 volume %. When the pore rate is less than 30 volume %, the retention amount of an electrolyte may decrease. When the pore rate is more than 80 volume%, the strength of the heat-resistant porous layer may become insufficient.

In view of the safety proof property as the heat-resistant porous layer, the thickness of the heat-resistant porous layer is suitably 2 to 30  $\mu\text{m}$ , more suitably 3 to 30  $\mu\text{m}$ . When the thickness is more than 30  $\mu\text{m}$ , the thickness including the shut-down layer becomes too thick as a separator for non-aqueous electrolyte secondary battery to obtain a high electric

capacity.

The separator for non-aqueous electrolyte secondary battery of the present invention has a spacer disposed on the external surface of a heat-resistant porous layer. The spacer has a form of particles, fibers, net or porous film, and suitably comprises an electrochemically stable substance.

The spacer is suitably an electrochemically stable organic polymer, in view of low price and light weight. The organic polymer can include an electrochemically stable inorganic compound. Moreover, shut-down function can be given also to the spacer by using a thermoplastic resin which softens at 80°C to 180°C. Although the shut-down temperature is higher than the operating temperature of battery, it is preferable to be lower in view of safety of a battery, and thermoplastic resins which soften at 80°C to 140°C can be used suitably.

In view of the electric capacity and the load characteristic of a battery, the thickness of the spacer is preferably as thin as possible, and suitably 5  $\mu\text{m}$  or less, more suitably 0.02  $\mu\text{m}$  to 5  $\mu\text{m}$ , and further suitably 0.02  $\mu\text{m}$  to 3  $\mu\text{m}$ .

Here, the thickness of a spacer means the difference of film thickness before and after providing a spacer to the external surface of the heat-resistant microporous layer. The thickness of a film is measured according to JIS K 7130.



The shape of the spacer is a form of particles, fibers, net or porous film. For example, a spacer having a form of fibers can be produced by arranging fibers comprising an organic polymer on a surface of the heat-resistant microporous layer. A spacer having a form of net can be produced by adhering a mesh-formed organic polymer to a surface of the heat-resistant microporous layer. A spacer having a form of porous film can be produced by adhering a non-woven fabric or microporous film comprising an organic polymer to a surface of the heat-resistant microporous layer. A spacer having a form of particles can be produced, for example, by coating and drying a suspension containing organic fine particles on a surface of the heat-resistant microporous layer. Among them, the spacer having a form of particles is industrially preferable, since a thin thickness spacer can be manufactured easily.

Especially, in a process of coating a suspension containing organic fine particles, the particles will be arranged as at least one layer on the surface of the heat-resistant porous layer. Supposing that particles having a diameter of  $3\text{ }\mu\text{m}$  are arranged as one layer, the thickness of the spacer will be  $3\text{ }\mu\text{m}$ . The particles do not need to be coated on whole of the surface of the heat-resistant porous layer completely, and the particles do not need to be adjacent to each other intensely.

The diameter of the particles is preferably 3  $\mu\text{m}$  or less. If the diameter exceeds 3  $\mu\text{m}$ , the thickness of the spacer will exceed 3  $\mu\text{m}$ , and the electric capacity or the load characteristic of the battery may be sometimes deteriorated. It is also possible to use two kinds or more of particles having different diameters. In order to prevent aggregation of the particles, it is preferable to mix two kinds or more of particles having different diameters.

Generally in a non-aqueous electrolyte secondary battery, a cathode sheet and an anode sheet are laminated with interposing a separator and rolled up spirally to form a rolled electrode. In the rolling up process, a part of a separator is first wound round a center core, and then, a cathode sheet and an anode sheet are supplied and rolled up with interposing the separator. Thus, the produced rolled electrode needs to be drawn out from the center core, but if the surface sliding property of the separator in contact with the center core is not sufficient, then an undue force is applied to the rolled electrode to cause a misalignment and unevenness in the electrode, and sometimes, breakage of the electrode may be caused.

As the center core, stainless steel is conventionally used, and it is suitable that the friction coefficient of the separator to stainless steel is low. The static friction

coefficient between the spacer-disposed separator and stainless steel whose surface is ground by a 1000 grit polishing paper, is measured according to JIS K7125. It is suitably 0.5 or less, and more suitably 0.3 or less.

When forming a spacer having a form of particles, fibers, net or porous film, the spacer does not necessarily need to be coated on the surface of the heat-resistant porous layer completely. Moreover, the degree of opening of the spacer having a form of particles, fibers, net or porous film is desirably large, in order to obtain excellent load characteristic of a battery.

Examples of the process for forming a spacer having a form of particles, fibers, net or porous film on the external surface of a heat-resistant porous layer include: laminating a non-woven fabric, a woven fabric, or a porous film on the external surface of the heat-resistant porous layer; forming a non-woven fabric on the external surface of the heat-resistant porous layer by a direct melt blow method, etc.; coating a polymer solution which may form a porous film, and the like.

The pore ratio of the shut-down layer or the heat-resistant porous layer is determined as follows.

A heat-resistant porous layer is cut off into a square of 10 cm, and the weight (Wg) and thickness (Dcm) are measured. The weight of the material in the sample is calculated, and the

weight of each material( $W_i$ ) is divided by true specific gravity to determine the volume of each material, and the pore ratio (volume %) is determined from the following formula.

Pore ratio (volume %)

$$= [1 - \{(W_1/\text{true specific gravity } 1) + (W_2/\text{true specific gravity } 2) + \cdots + (W_n/\text{true specific gravity } n)\} / (100 \times D)] \times 100$$

Examples of the electrochemically stable substances used for the spacer in the present invention include a substance which is molded into a porous film and used as a separator for lithium ion battery, but it is not deteriorated after being retained with applying a voltage of 4.2-4.5V for a long time.

Among them, suitably exemplified are organic polymers selected from the group consisting of: a polyolefin such as polyethylene and polypropylene; a polyolefin copolymer; a fluorine-containing polymer such as tetrafluoroethylene-hexafluoropropylene copolymer and polytetrafluoroethylene; a polycarbonate; an aromatic polyester; a polyethylene terephthalate; and celluloses such as carboxymethylcellulose and carboxyethylcellulose; or organic polymers thereof containing an electrochemically stable inorganic compound.

A fluorine-containing polymer such as tetrafluoroethylene-hexafluoropropylene copolymer and polytetrafluoroethylene and a cellulose such as

carboxymethylcellulose are preferable. The organic polymers thereof containing an electrochemically stable inorganic compound are also preferable, since it can be used an inorganic compound which can endure a voltage at which an organic substance cannot endure.

The separator in which a spacer is formed by coating an application liquid containing an electrochemically stable substance on the external surface of a heat-resistant porous layer is suitable from an industrial viewpoint, since the spacer is easily formed. Especially, to provide a spacer having a form of particles on the external surface of a heat-resistant porous layer, it is preferable that the application liquid is a suspension, since the thickness of the spacer can be made thin. Here, as the suspension, the suspension containing particles of an organic polymer is exemplified.

In the present invention, either of the heat-resistant porous layer, the shut-down layer and the spacer may contain an inorganic compound. The inorganic compound contained in a spacer may be just a high order metal oxide having an electrochemical-oxidation resistance, and inactive to an electrolyte. As a concrete example, although aluminum oxide, calcium carbonate, silica, etc. are exemplified, the present invention is not limited to these.

In the separator for non-aqueous electrolyte secondary

battery of the present invention, each layers may be simply piled on top of another, but in view of handling property, it is preferable to be bonded. As the method of bonding each layers, for example, the shut-down layer to the heat-resistant porous layer, and the heat-resistant porous layer to the spacer, a method by adhesive, a method by heat adhering, etc. are exemplified.

As for the separator of the present invention, examples of the process of coating an application liquid which contains an electrochemically stable substance on the external surface of a heat-resistant porous layer, and forming a spacer, are shown hereafter, but the present invention is not limited to these.

For example, a spacer can be formed on the external surface of a heat-resistant porous layer by a method containing the steps of following (a) - (c).

- (a) Preparing a suspension liquid comprising an electrochemically stable substance. When using an inorganic compound, a slurry liquid comprising a fine powdery inorganic compound is prepared, and mixed with the suspension liquid.
- (b) Coating the suspension liquid on a heat-resistant porous layer, and form an application layer.
- (c) Drying the application layer.

Moreover, a suitable piling method of the shut-down layer

and the heat-resistant porous layer is a piling process in which a microporous layer such as a porous film which is either a heat-resistant porous layer or a shut-down layer is used as a substrate, a solution layer is formed on the substrate by coating the another layer in a solution state and removing the solvent.

Examples of manufacture methods using a method of coating a heat-resistant resin solution and forming this heat-resistant porous layer on a shut-down layer are shown below, but the present invention is not limited to these.

For example, a heat-resistant porous layer can be formed on a shut-down layer by a method containing the steps of following (A) - (E).

(A) Preparing a solution comprising a heat-resistant resin and an organic solvent. When using an inorganic compound, a slurry liquid comprising a fine powdery inorganic compound in an amount of 1 to 200 parts by weight based on 100 g of the heat-resistant resin is prepared.

(B) Coating the suspension liquid or the slurry liquid on a shut-down layer, and form an application film.

(C) Depositing the heat-resistant resin in the application film.

(D) Removing the organic solvent from the application film.

(E) Drying the application film.

Here, as the organic solvent, a polar organic solvent is

usually used. As the polar organic solvent, for example, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone (hereinafter referred to as NMP), tetramethyl urea, or the like is exemplified.

The non-aqueous electrolyte secondary battery of the present invention is characterized by containing the separator described above.

In the non-aqueous electrolyte secondary battery of the present invention, a separator in which a spacer is placed adjacent to a cathode is preferable, since the heat-resistant porous layer adjacent to the spacer is hardly oxidized electrochemically.

Components other than the separator of the non-aqueous electrolyte secondary battery are explained below, but they are not limited to these.

As the nonaqueous electrolyte solution used in the non-aqueous electrolyte secondary battery of the present invention, for example, a nonaqueous electrolyte solution dissolving a lithium salt in an organic solvent can be used. As the lithium salt, exemplified are  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ , a lithium salt of lower aliphatic carboxylic acid,  $\text{LiAlCl}_4$ , etc. with being alone or a mixture in combination of two or more thereof. Among them, it is suitable to use at least one



containing fluorine selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ .

As the organic solvent used in the nonaqueous electrolyte solution of the present invention, for example, can be used are: carbonates such as propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, 4-trifluoromethyl-1,3-dioxolane-2-one, and 1,2-di(methoxy carbonyloxy)ethane; ethers such as 1,2-dimethoxyethane, 1,3-dimethoxypropane, pentafluoropropylmethylether, 2,2,3,3-tetrafluoropropyl difluoromethylether, tetrahydrofuran and 2-methyltetrahydrofuran; esters such as methylformate, methyl acetate, and  $\gamma$ -butyrolactone; nitriles such as acetonitrile, and butyronitrile; amides such as N,N-dimethylformamide, and N,N-dimethyl acetamide; carbamates such as 3-methyl-2-oxazolidone; sulfur containing compounds such as sulfolane, dimethyl sulfoxide, and 1,3-propane sultone; and the above solvents being introduced fluorine substituents. Usually, the above organic solvent can be used, with mixing two or more of these.

Among them, a mixed solvent containing a carbonate is suitable, and a mixed solvent comprising a cyclic carbonate and a non-cyclic carbonate or a cyclic carbonate and an ether are still suitable. As a mixed solvent of a cyclic carbonate and a non-cyclic carbonate, the mixed solvent comprising ethylene

carbonate, dimethyl carbonate, and ethyl methyl carbonate is suitable, at the point that the wide temperature range of operation, excellent load characteristic, and a hardly-decomposable property, even when a graphite material such as natural graphite and artificial graphite, is used as an active material for anode.

A cathode sheet used in the present invention is a sheet in which a composition containing a cathode active material, a conductive substance and a binder is supported on a current collector. Concretely, those which contain a material that can be doped/undoped with a lithium ion as the cathode active material, a carbonaceous material as a conductive substance, and a thermoplastic resin etc. as a binder can be used. As the material that can be doped/undoped with a lithium ion, exemplified are lithium composite oxide containing at least one sort of transition metals, such as V, Mn, Fe, Co, Ni and the like.

Among them, at the point that the average discharging electric potential is high, suitably exemplified are: a layered lithium compound oxide having  $\alpha$ -NaFeO<sub>2</sub> type structure as a matrix such as lithiated nickel dioxide and lithiated cobalt dioxide; and a lithium compound oxide having spinel type structure as a matrix, such as, spinel lithium manganese oxide.

The lithium composite oxide may also contain various

added elements, such as Ti, V, Cr, Mn, Fe, Co, Cu, Ag, Mg, Al, Ga, In and Sn. Especially when a composite lithiated nickel dioxide containing at least one of the above metal is used so that the above metal is to be 0.1-20% by mole, to the sum of the moles of the above metal and the moles of Ni in the lithiated nickel dioxide, the cycle property is improved in using at high capacity, and it is suitable.

Examples of thermoplastic resins as the binder include poly (vinylidene fluoride), copolymer of vinylidene fluoride, polytetrafluoroethylene, copolymer of tetrafluoroethylene-hexafluoropropylene, copolymer of tetrafluoroethylene-perfluoroalkyl vinyl ether, copolymer of ethylene-tetrafluoroethylene, copolymer of vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene, thermoplastic polyimide, carboxymethylcellulose, polyethylene, polypropylene, and the like.

Examples of carbonaceous materials as the conductive substance include natural graphite, artificial graphite, cokes, carbon black, and the like. The conductive substance can be used alone, and a composite conductive substance such as, for example, a mixture of artificial graphite and carbon black, can be used as well.

As the anode sheet in the present invention, for example, a material that can be doped/undoped with a lithium ion,

a lithium metal, or a lithium alloy can be used.

Examples of the material that can be doped/undoped with a lithium ion include: carbonaceous material, such as natural graphite, artificial graphite, cokes, carbon black, pyrolytic carbons, carbon fiber, and a fired products of organic polymer; chalcogen compounds such as oxides or sulfides which perform doping/undoping of lithium ion at an electric potential lower than the cathode. As the carbonaceous material, a carbonaceous material comprising a graphite material, such as natural graphite and artificial graphite as a main component is suitable, at the point that a big energy density is obtained when it is combined with a cathode, since the potential flatness is high, and the average discharge electric potential is low.

As the anode current collector used by the non-aqueous electrolyte secondary battery of the present invention, Cu, Ni, stainless steel, etc. can be used. Especially in a lithium secondary battery, Cu is preferable, since it hardly make an alloy with lithium and it is easy to process into a thin film. As a process for supporting the composition containing anode active material on the anode current collector, exemplified are: a method of carrying out press molding; and a method comprising the steps of making paste with using a solvent, coating on a current collector, drying, and press bonding.

The lithium secondary battery of the present invention is not particularly limited in shape and may have any one of the shapes such as a paper-sheet shape, a coin-like shape, a cylindrical shape and a rectangular parallelepiped shape.

#### EXAMPLES

Hereafter, although the present invention is explained by the examples still in detail, the present invention is not limited to these at all.

##### (1) Inherent viscosity

The flow time was measured at 30°C with a capillary viscometer, with respect to 96 to 98% sulfuric acid and a solution obtained by dissolving 0.5 g of the para-aramid polymer in 100 ml of 96 to 98% sulfuric acid. The inherent viscosity was then calculated from the ratio of the observed flow time according to the equation given below:

$$\text{Inherent Viscosity} = \ln(T/T_0)/C \text{ [unit: dl/g]}$$

where T and T<sub>0</sub> denote the flow time of the sulfuric acid solution of para-aramid and sulfuric acid, respectively, and C represents the para-aramid concentration (g/dl) in the sulfuric acid solution of para-aramid.

##### (2) Gas permeability

Gas permeability was measured according to JIS P 8117.

##### (3) Film thickness

Film thickness was measured according to JIS K 7130.

(4) Static friction coefficient

The static friction coefficient of the film to stainless steel whose surface is ground by a 1000 grit polishing paper was measured according to JIS K7125.

(5) Load characteristic of battery

In order to evaluate the performance of a battery using the separator, a plate battery was prepared as described below, and the load characteristic was measured.

In NMP, 3 parts by weight of poly(vinylidene fluoride) was dissolved, 9 parts by weight of artificial graphite powder and 1 part by weight of acetylene black as conductive substances, and 87 parts by weight of lithiated cobalt dioxide powder as a cathode active material were dispersed and kneaded to result a cathode composition paste. This paste was coated on aluminum foil with a thickness of 20  $\mu\text{m}$ , which is a current collector, dried and pressed by a roll to obtain a cathode sheet electrode.

This cathode sheet and a lithium metal as an anode are piled so that the separator is placed adjacent to the cathode sheet through the separator coated with the spacer. A plate battery was produced by adding an electrolyte in which 1M of  $\text{LiPF}_6$  was dissolved to a mixed solvent of 30 volume % ethylene carbonate, 35 volume % ethylmethyl carbonate, and 35 volume % dimethyl carbonate.

As for the resultant plate battery, constant current/constant voltage charging and constant current discharging was carried out under the following condition, and load characteristic of the battery was evaluated.

The load characteristic is represented by the value defined by "(Discharging capacity of charging/discharging X) / (Discharging capacity of charging/discharging Y)".

In the above, the conditions of charging/discharging X are:

maximum charging voltage: 4.3V

charging time: 8 hours

charging current:  $0.5\text{mA}/\text{cm}^2$

minimum discharging voltage: 3.0V, and

discharging current:  $0.5\text{mA}/\text{cm}^2$ .

The conditions of charging/discharging Y are:

maximum charging voltage: 4.3V

charging time: 8 hours

charging current:  $0.5\text{mA}/\text{cm}^2$

minimum discharging voltage: 3.0V, and

discharging current:  $10\text{mA}/\text{cm}^2$ .

#### (6) Evaluation of electrochemical oxidation resistance

In the same manner as the evaluation of load characteristic of battery, a plate battery was prepared, and constant current and constant voltage charging was conducted

under following conditions.

maximum charging voltage: 4.5V

charging time: 24 hours, and

charging current: 0.5mA/cm<sup>2</sup>.

After the charging, the battery was disassembled, and the separator was taken out and observed.

#### Example 1

1. Application of a heat-resistant porous layer, and production of a separator

##### (1) Synthesis of para-aramid solution

Poly(para-phenylene terephthalamide) (hereinafter referred to as PPTA) was synthesized in a 5-liter separable flask equipped with an agitating blade, a thermometer, a nitrogen flow-in pipe, and a powder inlet. In the flask sufficiently dried, 272.65 g of calcium chloride dried at 200°C for two hours were added to 4200 g of NMP. The flask was then heated to 100°C. The flask was cooled down to room temperature after complete dissolution of calcium chloride, and 132.91 g of para-phenylene diamine (hereinafter referred to as PPD) were added and completely dissolved. While the solution was kept at the temperature of  $20 \pm 2^\circ\text{C}$ , 243.32 g of terephthalic acid dichloride (hereinafter referred to as TPC) were added in ten portions at approximately 5 minutes intervals. The solution was kept at a temperature of  $20 \pm 2^\circ\text{C}$  for one hour for maturation



and then stirred under reduced pressure for 30 minutes for elimination of air bubbles. The polymer solution obtained showed optical anisotropy. A part of the polymer solution was sampled, and polymer was taken from the sampled polymer solution re-precipitated in water. The observed inherent viscosity of the PPTA thus obtained was 1.97 dl/g.

Then, 100 g of the polymer solution was added in a 500 ml separable flask with an agitating blade, a thermometer, a nitrogen flow-in pipe, and a powder inlet, and NMP solution was added gradually. Finally, PPTA solution having a PPTA concentration of 2.0 % by weight was prepared and referred as "P solution".

(2) Application of a para-aramid solution and production of a separator

As a shut-down layer, a porous film of polyethylene (film thickness of 25  $\mu\text{m}$ , gas permeability of 700 sec/100cc, average pore radius of 0.04  $\mu\text{m}$  (mercury porosimetry) was used. A film-like material of "P solution" which is a heat resistant resin solution was coated on the porous film put on a glass plate with a bar coater (clearance 200  $\mu\text{m}$ : produced by Tester Sangyo Co., Ltd.). After keeping this as it was, in a draft in a laboratory, for about 3 minutes, PPTA was precipitated and a clouded film-like material was obtained. The film-like material was immersed in ion-exchange water. After 5 minutes, the

film-like material was peeled off from the glass plate. After washing the material sufficiently with a flow of ion-exchange water, the free water was wiped away. The film-like material was sandwiched in Nylon sheet, and further in felt made of aramid. As in the state that the film-like material was sandwiched in Nylon sheet, and felt made of aramid, an aluminum plate was put on, a Nylon film was covered thereon, the Nylon film and the aluminum plate were sealed with gum, and a pipe for reducing pressure was attached. The whole was put in a heating oven, and the film-like material was dried with reducing pressure at 60°C, and a composite film comprising a porous film of polyethylene and a porous layer of aramid (thickness 5  $\mu$ m) was obtained.

## 2. Evaluation of shut-down function

The produced composite film was cut off in 40mm square, sandwiched between electrodes made of stainless steel each having 18mm  $\phi$  and 90mm square. A test battery was produced by adding an electrolyte in which 1M of LiPF<sub>6</sub> was dissolved to a mixed solvent of 30 volume % ethylene carbonate, 35 volume % ethylmethyl carbonate, and 35 volume % dimethyl carbonate. Applying a voltage of 1V at 1kHz between the electrodes, the electric resistance of the test battery was measured. The test battery was placed in an electric oven, and the temperature was raised at a rate of 2°C/minute from 25°C to 200°C, with measuring electric resistance. In this process, the temperature at which

electric resistance increases was observed as the shut-down actuation temperature.

The electric resistance at 25°C was 20  $\Omega$ . When the temperature of the battery was raised, electric resistance value rose abruptly near 140 °C to show 10k $\Omega$ . It was confirmed that the shut-down function actuates for this sample.

### 3. Application of a spacer

The composite film produced in Example 1, Section 1, was placed on a glass plate, a polypropylene suspension [product of Mitsui Chemicals Inc.; Chemipearl WP100, particle diameter of 1  $\mu$ m (measured by coal tar counter method)] by adjusting the solid concentration to 20% with adding ion-exchanged water, was coated on the surface of the aramid porous layer side, with a bar coater (clearance 10  $\mu$ m: produced by Tester Sangyo Co., Ltd.), and dried in air. The thickness of the spacer was 1  $\mu$ m.

The evaluation result of the separator is shown in Table 1.

### Example 2

The composite film produced in Example 1, Section 1, was placed on a glass plate, a polyethylene suspension [product of Mitsui Chemicals Inc.; Chemipearl W950, particle diameter of 0.6  $\mu$ m (measured by coal tar counter method)] by adjusting the solid concentration to 20% with adding ion-exchanged water, was

coated on the surface of the aramid porous layer side, with a bar coater (clearance 10  $\mu$ m: produced by Tester Sangyo Co., Ltd.), and dried in air. The thickness of the spacer was 1  $\mu$ m.

The evaluation result of the separator is shown in Table 1.

#### Example 3

The composite film produced in Example 1, Section 1, was placed on a glass plate, a suspension produced by mixing a polyethylene suspension [product of Mitsui Chemicals Inc.; Chemipearl W950, particle diameter of 0.6  $\mu$ m (measured by coal tar counter method)] and a suspension of tetrafluoroethylene-hexafluoropropylene copolymer [product of Daikin Industries Ltd.; ND-1, particle diameter of 0.1-0.25  $\mu$ m] in a solid ratio of 2:1, and adjusting the solid concentration to 20% with adding ion-exchanged water, was coated on the surface of the aramid porous layer side with a bar coater (clearance 10  $\mu$ m: produced by Tester Sangyo Co., Ltd.), and dried in air. The thickness of the spacer was 1  $\mu$ m.

The evaluation result of the separator is shown in Table 1.

#### Example 4

The composite film produced in Example 1, Section 1, was

placed on a glass plate. A carboxymethylcellulose [product of Dai-ichi Kogyo Seiyaku Co., Ltd.; Cellogen 4H] was dissolved in ion-exchanged water, and alumina fine powder [product of Nippon Aerosil Co., Ltd.; Alumina C, particle diameter of 0.013  $\mu\text{m}$ ] were dispersed therein, then the solid concentration was adjusted to 1.5% with adding ion-exchanged water. The solution was coated on the surface of the aramid porous layer side, and dried in air. The thickness of the spacer was 1  $\mu\text{m}$ .

The evaluation result of the separator is shown in Table 1.

#### Comparative Example 1

A composite film of Example 1, section 1 was evaluated without forming a spacer. The evaluation result of the separator is shown in Table 1.

Table 1

	Electrochemical oxidation resistance	Load characteristic	Static friction coefficient
Example 1	No color change	52%	0.40
Example 2	No color change	58%	0.41
Example 3	No color change	68%	0.19
Example 4	No color change	68%	0.44
Comparative Example 1	Color change	69%	0.59

The separator for non-aqueous electrolyte secondary battery of the present invention has a shut-down function and heat-resistance, and excellent electrochemical oxidation resistance as well. Even if a heat generation occurs by accident, it is possible to suppress the heat generation under a certain amount, and a battery having improved safety can be obtained. The battery using the separator of the present invention has excellent properties as a battery, and the separator can be produced easily by forming a spacer with an application method, the industrial value is large.